Steam Reforming
of
Low-Level Mixed Waste

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Introduction

The U.S. Department of Energy (DOE) is responsible for the treatment and disposal of an inventory of approximately 160,000 tons of Low-Level Mixed Waste (LLMW). Most of this LLMW is stored in drums, barrels and steel boxes at 20 different sites throughout the DOE complex. The basic objective of low-level mixed waste treatment systems is to completely destroy the hazardous constituents and to simultaneously isolate and capture the radionuclides in a superior final waste form such as glass. The Department of Energy (DOE)[1] is sponsoring the development of advanced technologies that meet this objective while achieving maximum volume reduction, low-life cycle costs and maximum operational safety. ThermoChem, Inc. is in the final stages of development of a steam-reforming system capable of treating a wide variety of DOE low-level mixed waste that meets these objectives. The design, construction, and testing of a nominal 1ton/day Process Development Unit (PDU) is described.

Objectives

Historically, very few acceptable options have been available for the treatment of LLMW. Concerns over the safety of incineration systems have limited their applicability. An advanced treatment system is needed that totally destroys the hazardous components in LLMW, without incineration, and produces a non-leachable final waste form that can be readily and safely disposed of at a licensed low-level burial site. Steam reforming provides unique characteristics for meeting these objectives for a major portion of the DOE LLMW. In the steam-reforming reaction, steam reacts with hydrocarbons in the feed to predominantly produce carbon monoxide and hydrogen, commonly called synthesis gas.

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ThermoChem and MTCI have conducted extensive pilot- and demonstration-scale steam reforming tests of various waste materials including, waste oil, sewage sludge, paper mill sludge, black liquor, refuse-derived fuel, and agricultural waste. The ThermoChem/MTCI patented steam-reforming technology is being applied commercially to the processing of black liquor in the world pulp and paper industry. Black liquor is a caustic liquid containing resin and lignin hydrocarbons and sodium carbonate. In the black liquor application, the hydrocarbons in the liquor are converted to synthesis gas and the sodium carbonate is recovered for reuse in the papermaking process. Because of its ability to remove and convert hydrocarbons to synthesis gas, including halogenated and non-halogenated hazardous compounds, while isolating inorganic material including the radionuclides found in LLMW, the DOE is sponsoring a program to demonstrate the performance of the ThermoChem/MTCI steam-reforming system to LLMW surrogates representative of those found in the DOE inventory. An option under the contract provides for a detailed design of a 100 to 500 lb/hour unit that could be fabricated and tested on actual LLMW at a chosen DOE site.

Project Description

Under the DOE contract, ThermoChem and its subcontractors, Manufacturing and Technology Conversion International, Inc. (MTCI); Thermatrix, Inc.; Stone & Webster Engineering Corporation; and the Clemson Vitrification Research Laboratory are to design, build and operate a nominal 2,200 pound per day Process Development Unit (PDU) and to conduct extensive tests on six LLMW surrogate waste feeds to verify hazardous component destruction and the isolation and capture of radioisotopes. Also, solid inorganic material from the steam reformer PDU test runs will be incorporated into different glass formulations and leachability tests will be conducted. MTCI is responsible for PDU process design, fabrication and testing; Thermatrix is the supplier for the flameless oxidizer and gas cleanup subsystem; Stone & Webster Engineering is responsible for structural and layout design; and Clemson Vitrification Research Laboratory is responsible for conducting vitrification tests.

The ThermoChem/MTCI steam-reforming system for the treatment of LLMW is depicted in *Figure 1*. The PDU consists of the following major subsystems:

- Solid/liquid feeding system,
- First-stage fluidized bed steam reformer with internal cyclone,
- HEPA filter for fines capture,
- Second-stage steam reformer,
- Flameless thermal oxidizer,
- Gas cleanup containing:
    - spray cooler/dry scrubber
    - soda ash and water solution feed system for scrubber
    - Baghouse and HEPA filters
    - polishing wet scrubber
    - activated carbon filter
    - induced draft fan, and
- Boiler and super heater.

The first-stage steam reformer is an indirectly heated fluidized bed in a refractory-lined reactor vessel. The fluidizing medium is steam for superior mixing and heat transfer to the material to be treated. Electrical heaters immersed in the bed provide supplemental heat as required. The bed temperature is very closely controlled to ensure complete volatilization and partial steam reforming of all organic compounds and to ensure retention of radionuclides, including cesium compounds in solid form, along with other inorganics in the bed. The first stage is continuously fed waste material using a Moyno pump subsystem for liquids and sludges and/or a metered screw feed with lockhoppers for solid material. Glass frit or sand is added to the bed as needed if the final waste form is to be glass. Sand or glass frit is also used as the start-up bed material. The inorganics left in the reactor, including radioactive material, are continuously removed and collected in sealed containers. With the exception of larger inorganic chunks that may be in the feed material, the bed material will be a nominal 250 micron mean size material. The final waste form can be glass, metal or a high-integrity container depending upon radiation levels and leachability requirements. For most of the DOE LLMW, glass is anticipated to be the final waste form.

An internal cyclone and a high-temperature pulse jet HEPA filter at the exit of the first stage steam reformer serves to essentially eliminate the carryover of particulates in the synthesis gas stream. After particulate removal, the synthesis gas flows into a Thermatrix flameless thermal oxidizer. This non-incineration system converts the carbon monoxide, hydrogen and hydrocarbon vapors into water and carbon dioxide and acid gases. A second-stage, higher temperature steam reformer is available upstream of the thermal oxidizer and can be used if needed to ensure higher Destruction and Removal Efficiencies (DRE). Based on laboratory testing, it is believed that the ThermoChem/MTCI overall system will achieve 99.9999 percent DRE for the Principal Organic Hazardous Constituents (POHCs) found in DOE wastes. A gas cleanup system removes acid gases as dry salts followed by an activated carbon filter as a final polishing step. Negative pressure is maintained throughout the entire system by the induced draft fan.

The surrogate feedstock formulations to be tested are shown in *Table 1*. During the testing period, different temperatures and feed rates will be evaluated and DRE and radionuclide retention will be assessed.

Accomplishments

In preparation for extensive tests of surrogate materials in the PDU, screening tests were performed in a smaller steam reformer test unit with ion exchange resins to acquire operating experience and collect preliminary data on performance. Ion exchange resins are a part of each of the six surrogate feedstocks. Specifically, the objective was to determine how well the surrogate cesium is retained in the bed solids and to determine the concentration of surrogate cesium in the synthesis gas stream, if any. *Figure 2* depicts the test unit used in the screening tests. The system consists of a pulse combustor with two U-shaped tailpipes (fluidized bed heat source), super-heater (fluidizing steam source), fluidized bed reactor, air-tight screw feeder, two cyclones, flare, venturi scrubber, ID fan and stack. The pulse combustor supplies heat to both the reactor and superheater. The resin vaporizes, devolatilizes, and undergoes steam-reforming reactions in the fluidized bed. The pulse combustor supplies the endothermic heat of reaction and its firing rate can be adjusted to operate the fluidized bed in the temperature range between 1000°F and 1600°F. The synthesis gases (rich in hydrogen) pass from the reactor through two cyclones to the flare where they are burned out by a natural-gas burner flame. Gases exiting the flare and superheater pass through the venturi scrubber and are conveyed to the stack by the ID fan.

Several short shakedown tests were performed on the system with and without resin feed to verify operability. Two 55-gallon drums of spent utility ion exchange resin and 1.5 kg of cesium chloride were acquired for the screening test. Analysis of the resin is presented in *Table 2*. To prepare surrogate waste, cesium chloride (CsCl) was thoroughly dissolved in distilled water and the solution was mixed with resin. The mixture stayed in the MTCI laboratory for 24 hours for CsCl adsorption by resin. The water was drained afterwards and the CsCl-doped resin was spread on a large flat surface for air drying.

At the beginning of the test, 131 pounds of silica sand (200 to 300 microns size) were loaded into the reactor. The reactor temperatures and pressures were monitored to verify stable operation. Sixty pounds of doped resin were fed to the steam reformer over a period of approximately five hours. The mean bed temperature during the test was regulated to about 1050°F. In order to determine surrogate cesium carryover, an isokinetic sampling probe was located in the straight pipe downstream of the second cyclone. The gas sample passed through a 5 micron pore size sintered metal filter and a 12-inch high column of distilled water. Two gas samples were taken during the test at 20-minute intervals. A total isokinetic sampling time of 35 minutes was used to collect solids in the sintered metal filter for analysis.

Following is the full list of samples sent for analyses:

- Pure resin, ultimate analysis;
- CsCl doped resin, analysis for Cs content;
- Bed drain sample, analysis for Cs content;
- Cyclone catch sample, analysis for Cs content;
- Solids collected in the sintered metal filter, analysis for Cs and other metals content;
- Condensed water sample, analysis for Cs and other metals content;
- Two gas samples taken downstream of water bath, analysis for Cs content; and
- Bed drain sample, ultimate analysis.

A total of 0.1248 pound of cesium was fed and a total of 0.1152 pound was collected, yielding 92.3 percent mass balance. This is short of the 100 percent desired and is due to solids left undrained in the first cyclone dipleg. The cesium concentration in the gas samples collected from the sampling train was below the detection limit of 1 part per billion. This strongly indicates that all cesium is in the solid bed material and the only cesium that would be lost in a system would be that escaping the HEPA filtering and scrubbing system. Therefore, the PDU should essentially retain all of the cesium fed. This result is very encouraging.

A total of 38.012 pounds of carbon were fed and a total of 12.904 pounds of carbon were collected in the solids, yielding a carbon conversion of 66.1 percent. This results in a mass reduction of over 10 to 1. This is consistent with data for steam reforming of various feedstocks at low temperatures. For example, the carbon conversion for steam reforming black liquor at 1065ºF turns out to be on the order of 60 percent.

In summary, the screening test was successful and pointed out that (i) cesium can essentially be retained in the solids, (ii) organics, sulfur and chlorine can be separated from the solids stream, and (iii) significant volume and mass reduction can be achieved.

Future Activities

Extensive PDU tests on six types of low-level mixed waste surrogates will be conducted in November and December 1996. Follow-on efforts include detailed design of a steam-reforming system for testing on radioactive material at a DOE site.

Acknowledgments

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FIGURE 1: THERMOCHEM/MTCI STEAM-REFORMING SYSTEM FOR TREATMENT OF LOW-LEVEL MIXED WASTE

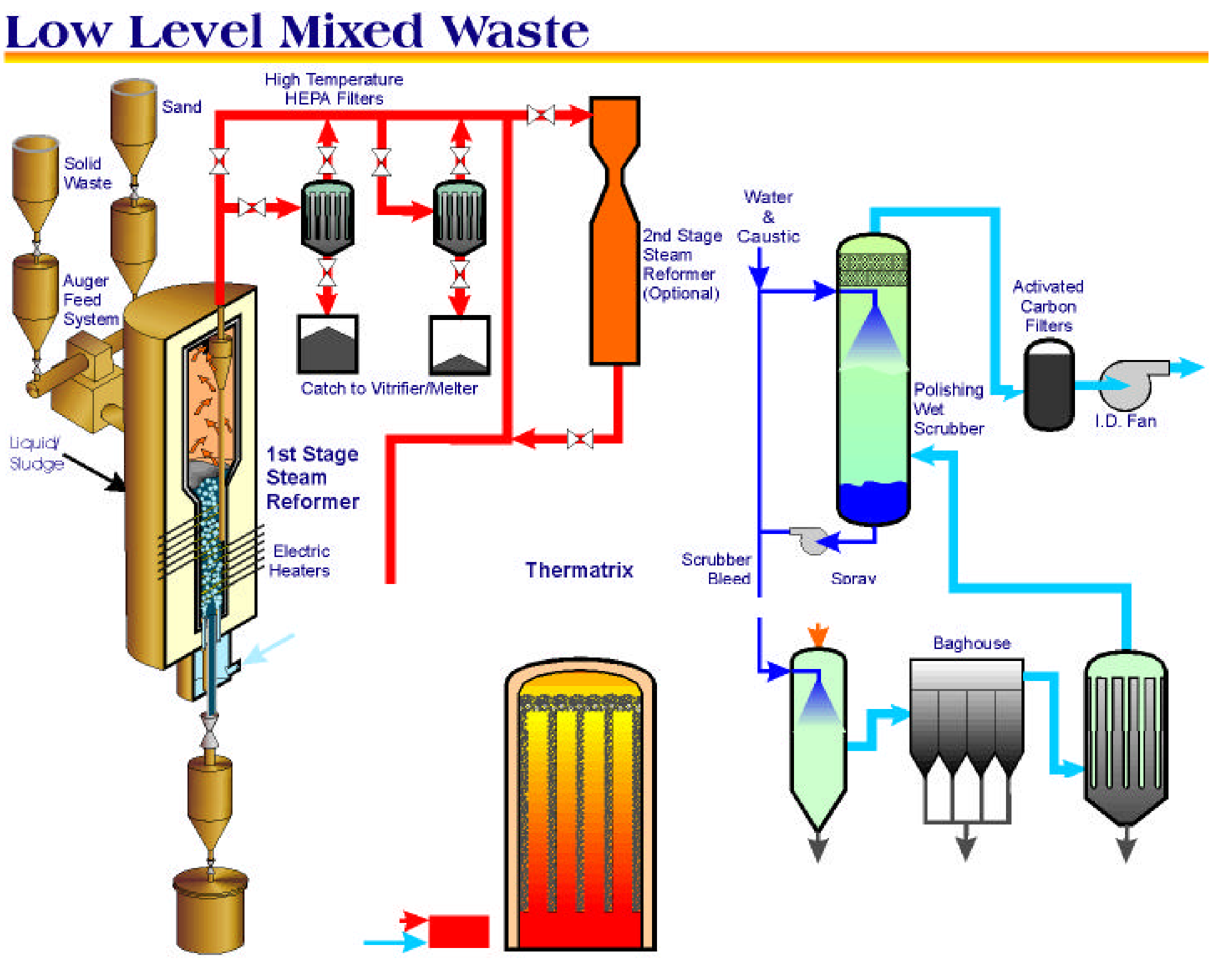

FIGURE 2: TWO-TUBE REACTOR PROCESS FLOW DIAGRAM

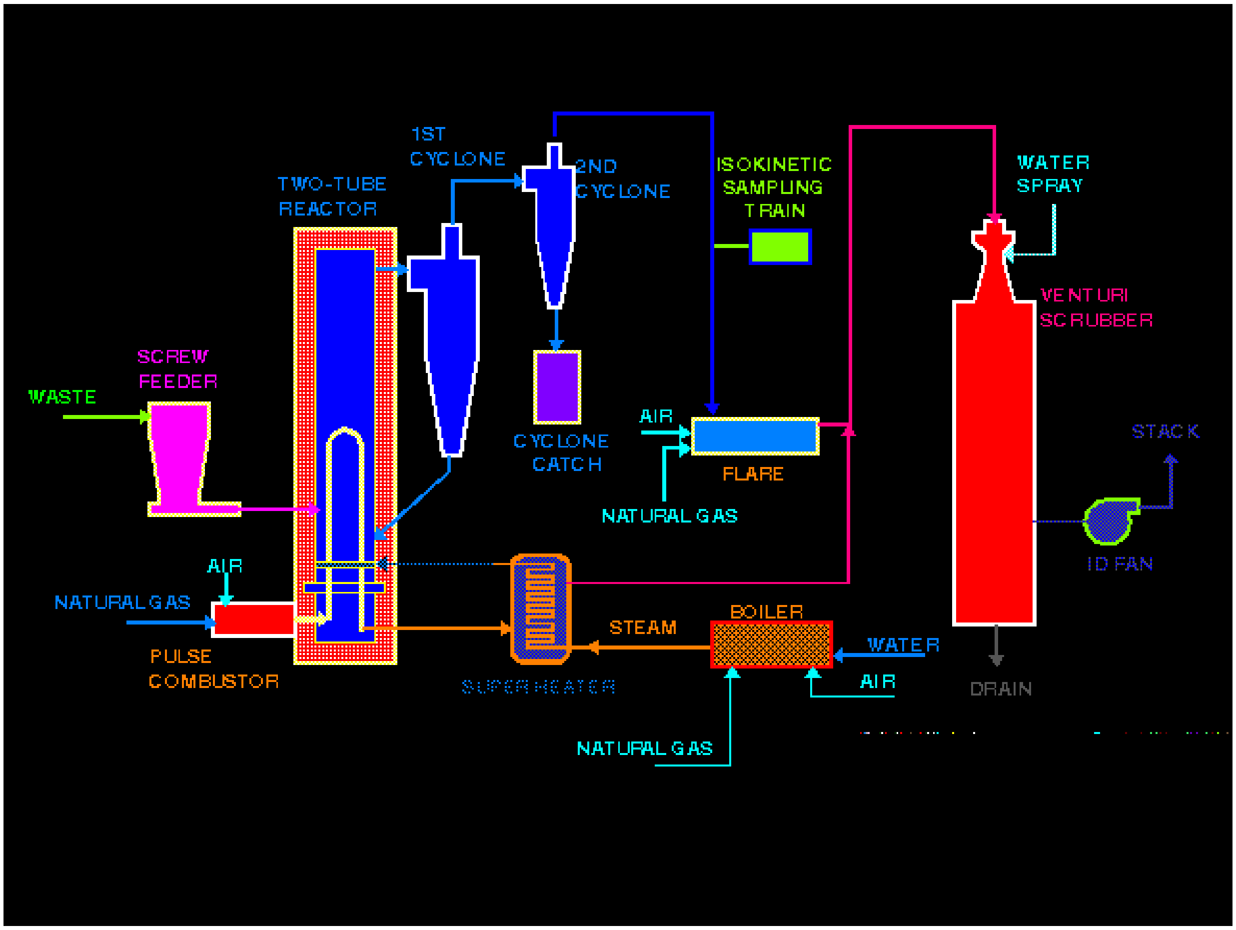

TABLE 1:

SURROGATE FORMULATION - SUMMARY

Number / Component	Heterogeneous Debris	Aqueous Halogenated Organic Liquids	Absorbed Aqueous Organic Liquids	High Organic Content Sludges	Cement, Sludges, Ashes & Solids	Natural Aqueous Wastes
	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%
Bulk Ingredient 1. Activated Carbon	5.	5.	5.	10.	10.	5.
2. Cation Exchange Resin	5.	5.	5.	5.	5.	5.
3. Water	10.	10.	19.	15.	30.	75.
4. Wood	10.					
5. Polyvinylchloride (PVC)	10.					
6. Neoprene	10.					
7. Mild Steel / Hematite / Fe_2O_3	10.			10.	3.	
8. Glass Beads	10.					
9. Cement / Concrete	8.					
10. Alumina / Al_2O_3	10.			5.	2.	
11. Diatomaceous Earth	10.					
12. Toluene		10.				
13. Tetrachloroethylene		10.				
14. Mineral Oil		10.		7.		
15. Ethylene Glycol		10.	10.	10.		
16. Vermiculite		19.	25.			
17. Perlite (SiO_4)			25.	10.	10.	
18. $CaSO_4 \bullet 2H_2O$ / Plaster of Paris				10.	3.	
19. Phenol				10.		
20. Fly Ash (ASTM Class F)					15.	1.
21. Concrete (cured, crushed, screened)					20.	
22. $CaCl_2$						3.

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	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%
23. $NaHCO_3$ / $NaNO_3$ *						3.
24. $MgSO_4 \bullet 7H_2O$ / $Al(NO_3)_3$ *						3.
25. $Na_2HPO_4 \bullet 7H_2O$						3.
RCRA Metals 26. $Cr(NO_3)_2 \bullet 6H_2O$ (or oxide)	0.1	0.1	0.1	0.1	0.1	0.1
27. $Ni(NO_3)_2 \bullet 6H_2O$	0.1	0.1	0.1	0.1	0.1	0.1
28. $Pb(NO_3)_2$	0.1	0.1	0.1	0.1	0.1	0.1
29. $Cd(NO_3)_2 \bullet 4H_2O$	0.1	0.1	0.1	0.1	0.1	0.1
RCRA Organics 30. Naphthalene ($C_{10}H_8$)	0.5	10.	5.	2.	0.5	0.5
31. 1,2-Dichlorobenzene ($C_6H_4Cl_2$)	0.5	10.	5.	5.	0.5	0.5
Radionuclide Surrogate 32. $CeCl_3$	0.3	0.3	0.3	0.3	0.3	0.3
33. $CsCl$ / $CsNO_3$	0.3	0.3	0.3	0.3	0.3	0.3

* Suggested substitute for surrogate Feedstock No. 6 only.

Table 2
Analysis of Resin Feed

	FED
Total	206
Sand	131
Pure Wet Resin	15
Doped Dry Resin	60
Total Resin including:	75
Moisture	10.509
Ash	1.29
Carbon	38.0115
Sulfur	4.455
Hydrogen	4.272
Nitrogen	3.4845
Oxygen	12.978
Cesium	0.1248